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**Notes:**

1. Untranslatable words are replaced with asterisks (\*\*\*\*).
2. Texts in the figures are not translated and shown as it is.

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**CLAIM + DETAILED DESCRIPTION**

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**[Claim(s)]**

[Claim 1] It faces carrying out antiphase suspension polymerization of the water-soluble ethylene nature unsaturation monomer, and manufacturing absorptivity resin. Using a water-soluble radical polymerization initiator, give a water-soluble ethylene nature unsaturation monomer aqueous solution to the antiphase suspension-polymerization reaction of the water-in-oil type of the first step under existence of a cross linking agent among the bottom hydrophobic organic solvent of existence of an emulsifier if needed, and subsequently Are seven or more HLB and the nonionic surface active agent of HLB higher than HLB of said emulsifier, anionic surface active agents or these mixtures, and a water-soluble ethylene nature unsaturation monomer aqueous solution are added in the polymerization reaction system of the first step. The manufacture method of the absorptivity resin characterized by repeating operation of performing an additional antiphase suspension-polymerization reaction, once or more after making the water polymer gel grains which generated this aqueous solution absorb.

[Claim 2] The method according to claim 1 of adding the water-soluble ethylene nature unsaturation monomer aqueous solution to add on the occasion of the polymerization of dibasic stage henceforth, so that the temperature of the reaction mixture after the absorption treatment to this polymer gel grain of this aqueous solution may become below in the decomposition temperature of a water-soluble radical polymerization initiator.

[Claim 3] The method according to claim 1 of making dissolve or mix with the water-soluble ethylene nature unsaturation monomer aqueous solution to which the surface active agent to add is added on the occasion of the polymerization of dibasic stage henceforth, and adding.

[Claim 4] The method according to claim 1 of adding the water-soluble ethylene nature unsaturation monomer aqueous solution to add in the polymerization reaction system of the preceding paragraph on the occasion of the polymerization of dibasic stage henceforth at 5 to

300weight % of a rate of the water-soluble ethylene nature unsaturation monomer aqueous solution of the first step.

[Claim 5] The way according to claim 1 a water-soluble ethylene nature unsaturation monomer consists of one sort or two sorts or more of mixtures chosen from acrylic acid or its salt, methacrylic acid or its salt, acrylamide, and methacrylamide.

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#### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture method of absorptivity resin. This invention relates to the method of manufacturing bead-like absorptivity resin with a big grain size, in detail by adding and polymerizing a specific surface active agent and said specific monomer in the water polymer gel obtained by having made carry out antiphase suspension polymerization of the water-soluble ethylene nature unsaturation monomer. Since according to the manufacture method of this invention the agglomerated material which with a mean particle diameter [ 200-3000micro ] product agglomerated material was obtained arbitrarily, and was obtained has few fines, and its particle size distribution is narrow, and the binding capacity of a primary particle is large and speed of water absorption is still larger, It can be used for dominance as engineering works or structural materials as the field for agriculture and also water cutoff material, lubricant, dew condensation prevention material, etc. not only as hygienic goods, such as a disposable diaper and a physiology napkin, but as a soil water retention agent.

[0002]

[Description of the Prior Art] Absorptivity resin is used for industrial ways, such as not only hygienic goods, such as a disposable diaper and sanitary items, but water cutoff material, dew condensation prevention material, a freshness holding material, solvent dehydration material, etc., tree planting, a plantation art use, etc., and the thing of former versatility is proposed in recent years. As this kind of absorptivity resin, a hydrolyzate [ of a starch-acrylonitrile graft copolymer ], carboxymethylcellulose bridge formation object, bridge formation polyacrylic acid (salt), and acrylic acid (salt)-vinyl alcohol copolymer, bridge formation polyethylene oxide, etc. are known.

[0003] However, these absorptivity resin was hard to be called what each can satisfy in a grain size. There were various problems in the polymer obtained especially by antiphase suspension polymerization. For example, in water-in-oil type (W/O type is called below) antiphase suspension polymerization of an acrylic acid alkali metal salt, The sorbitan fatty acid ester of HLB 3-6 given [ as a dispersant ] in JP,S54-30710,B, When the Nonion system surface active agent of HLB 6-9 given in JP,S57-167302,A or the surface active agent of HLB8-12 given in

JP,S60-25045,B was used, as for all, only absorptivity resin with a as fine grain size as about ten to 100 micrometer was obtained. When an oleophilic carboxyl group containing polymer is used for a dispersant JP,S63-36321,B and given in JP,S63-36322,B on the other hand, Although the polymer whose grain size is about hundreds of micrometers was obtained, since the compatibility of a dispersant and an acrylic acid system monomer was high, there was a problem of being easy to agglomerate at the time of a polymerization reaction.

[0004] It is considered as how to enlarge the grain size of absorptivity resin, and is a dispersant in JP,H1-17482,B and JP,S57-158210,A. Although the method of using oil solubility cellulose ester or cellulose ether was shown, by such a method, the dispersant which remained at the time of desiccation fused, and there was a problem of polymer having condensed or being easy to adhere to a container wall. Moreover, when the polyglyceryl fatty acid ester of HLB2-16 is used for a dispersant given in JP,S62-172006,A, Though the polymer of the diameter of a large drop is obtained, since the tolerance level of the conditions of manufacture for obtaining it stably was very narrow, when it separated from this condition, and it was easy to cause block polymerization and industrial stable production was taken into consideration, it was hard to call it an advantageous thing.

[0005] On the other hand, the method of granulation-izing the primary particle of absorptivity resin, using binders, such as water and polyvinyl alcohol, as a method of replacing above is proposed. However, there is a problem that what uses water as a binder in this method will have the very weak binding property of grains, and binding grains will break easily at the time of general conveyance or handling. Moreover, although a binding property is improved, since it needed a lot of polyvinyl alcohol and it needed special equipment, what uses polyvinyl alcohol became a cost overrun, and it was not necessarily a predominant technique.

[0006] Moreover, make the dispersing element in the non-aqueous liquid of the absorptivity resin seed grains formed from the first monomer form in JP,S62-230813,A, this grain is made to absorb a water-soluble ethylene nature unsaturation dibasic monomer, and the seed polymerization method which consists of subsequently polymerizing a dibasic monomer is shown. And according to this method, it is indicated that the absorptivity resin which has a bigger thing than seed grains and the large particle diameter which seed grains condensed is obtained. However, when polymerizing [ this method ] a dibasic monomer, in order to use the same dispersant (W/O type dispersant) or same stabilizer as the first monomer, When these are dissolving in a solvent and add a dibasic monomer aqueous solution in a system under this state, Before liquid absorption of the dibasic monomer aqueous solution is carried out to the hydrous gel grains obtained by the first-step polymerization, it will be in a suspension state and has the problem that the liquid absorption of the dibasic monomer to seed grains is very late, and the floc which was excellent in binding hardness is hard to be obtained.

[0007] On the other hand, in the same seed polymerization method as JP,H3-227301,A, cool

the slurry liquid after the first-step end of antiphase suspension polymerization, and a surface active agent and/or polymer protective colloid should be in a deposit state in a solvent. The manufacture method of absorptivity resin of carrying out, adding the monomer aqueous solution of eye the dibasic stage, and performing the polymerization of dibasic stage henceforth after liquid absorption is proposed. In order to deposit a surface active agent and/or polymer protective colloid by cooling the polymerization liquid of the first step by this method When the monomer aqueous solution of a surface activity function, i.e., eye the dibasic stage, does not form suspension, i.e., a W/O type emulsion, but liquid absorption is fully performed and this is polymerized, it is said that absorptivity [ with particle size distribution sharp moreover ] resin with few fines is obtained.

[0008] However, although this method aims at depositing a surface active agent by cooling and stopping a surface activity function, in the inside of a surface active agent and/or polymer protective colloid, it consists of tens of [ several to ] sorts of many components, and the deposit temperature of a constituent also actually differs considerably. therefore -- in order to deposit completely the substance which consists of such many components -- a case -- zero -- it is necessary to choose the following very severe conditions, and actually next to impossible. Therefore, it is actual to stop at the place which deposits an important component in practice, the W/O type surface active agent and/or polymer protective colloid which dissolved into suspension still more exist by this, and the liquid absorption of the monomer aqueous solution of eye the dibasic stage is checked remarkably. As a result, even if the absorptivity resin obtained by the method can do agglomerated material which the primary particle moreover condensed including remarkable fines, the binding hardness should be broad and should not be satisfied.

[0009] Moreover, in order for rate of adsorption to also be remarkably checked by cooling, to make sufficient absorption perform and to close it, tens of minutes - several hours are required. When following, for example, dealing with the very intense acrylic acid system monomer of polymerization nature, process time is long also in process and it is required, and the operation is very complicated and the danger for the unusual polymerization under liquid absorption is not only very high, but it inferior to productivity.

[0010] Moreover, the radical polymerization reactive surface active agent of specification [ JP,H6-184211,A ] It uses, the first-step polymerization is performed, the radical polymerization reactive surface active agent used for the first step is incorporated into seed polymer, and the method of vanishing a surface active agent from a medium is indicated by the liquid absorption of dibasic stage henceforth, and polymerization.

[0011]

[Problem(s) to be Solved by the Invention] By this method, the advantage which does not perform the superfluous surface active agent in a medium for cooling operation etc., but may

absorb the monomer of eye a dibasic time in high temperature comparatively is emphasized. [ also although it says that a specific radical polymerization reactive surface active agent is used although this method can be said to be a theoretical very interesting technique, substance is a remarkable non-polymerized thing's remaining and writing in this Description, but ] Protective colloid accompanied by an emulsifier as a dependent for stabilizing physically the reactant incorporated into suspension, For example, if the emulsification stability as a surface active agent is bad and independent as the usability of the polyethylene oxidized or reformed by modification cellulose and maleic anhydride or its copolymer is described, seed grains are not obtained stably. Therefore, this remains into a medium as a result, a W/O type emulsification system is formed also in the polymerization reaction system of dibasic stage henceforth, and a particle has the problem that and a satisfactory granulated body is not obtained.

[0012] The purpose of this invention is the manufacture method of absorptivity resin of the shape of a bead acquired by the above mentioned antiphase suspension-polymerization method, and there is in offering the method of manufacturing the agglomerated material with a big binding property which it is easy, and granulation efficiency is good, without depositing a surface active agent and/or polymer protective colloid, and has few particles.

[0013]

[Means for Solving the Problem] [ the reaction mixture which contains the water polymer gel grains obtained by antiphase suspension polymerization as a result of inquiring wholeheartedly, in order that this invention person etc. may solve said problem ] The Nonion system surface active agent, the anionic surface active agents, or these mixtures of HLB higher than HLB of the emulsifier which are seven or more HLB and is used for the first-step polymerization reaction are added, and a monomer aqueous solution is made to absorb (in addition). By [ which may be called "liquid absorption" instead of the following "absorption" ] \*\*\*\*\* (ing) The thing with few particles to the agglomerated material with which liquid absorption of the monomer aqueous solution was efficiently carried out to seed grains very early, and the an average of 200-3000micro product granulation article was obtained arbitrarily which has the big binding hardness of granulation grains and in which particle size distribution is narrow is obtained, Furthermore, it finds out that speed of water absorption is improved sharply, and came to complete this invention.

[0014] Namely, this invention is faced carrying out antiphase suspension polymerization of the water-soluble ethylene nature unsaturation monomer, and manufacturing absorptivity resin. Using a water-soluble radical polymerization initiator, give a water-soluble ethylene nature unsaturation monomer aqueous solution to the antiphase suspension-polymerization reaction of the water-in-oil type of the first step under existence of a cross linking agent among the bottom hydrophobic organic solvent of existence of an emulsifier if needed, and subsequently

Are seven or more HLB and the nonionic surface active agent of HLB higher than HLB of said emulsifier, anionic surface active agents or these mixtures, and a water-soluble ethylene nature unsaturation monomer aqueous solution are added in the polymerization reaction system of the first step. After making the water polymer gel grains which generated this aqueous solution absorb, it is the manufacture method of the absorptivity resin characterized by repeating operation of performing an additional antiphase suspension-polymerization reaction, once or more.

[0015] In this invention, the liquid absorption of a monomer aqueous solution can carry out in the first place efficiently very early by adding the aforementioned specific surface active agent to the reaction mixture containing the water polymer gel grains obtained in the water-soluble ethylene nature unsaturation monomer aqueous solution in the first step. Therefore, polymerization nature is intense, for example, an acrylic acid system monomer can also carry out addition liquid absorption to the slurry system of the first step in high temperature comparatively.

[0016] However it may raise churning by the polymerization of dibasic stage henceforth to the second, it will be hard to generate simple grain child-like fines polymer. On the other hand, like said JP,H3-227301,A, by the method of depositing a surface active agent, since a surface active agent is a multi-component system, the component which never deposits remains, this forms an emulsification system, and a particle occurs. It is [ third ] possible at temperature with arbitrary liquid absorption, for example, the cooling operation for a surface active agent deposit etc. is completely unnecessary like said JP,H3-227301,A. Mean particle diameter, binding hardness, etc. are arbitrarily changeable by fourth choosing the kind and quantity of a surface active agent suitably.

[0017] It is being able to take to the fifth in the range where the monomer aqueous solution liquid adsorption ratio of dibasic stage henceforth to the monomer aqueous solution of the first step is very large. That is, target granulation is possible at very little liquid absorption monomer aqueous solutions. In JP,H3-227301,A which is the conventional technology of the aforementioned seed polymerization method, the amount of minimums is 50% of the first step, and the monomer aqueous solution of dibasic stage henceforth has very bad granulation-ized efficiency as it is indicated that desired various effects cannot be discovered by less than this in this gazette. the variety of \*\* -- the product agglomerated material obtained [ sixth ] by this invention has very early speed of water absorption -- it has the busy feature. Each constituent elements of this invention are explained in detail hereafter.

[0018] (Water-soluble ethylene nature unsaturation monomer) Fundamentally, the water-soluble ethylene nature unsaturation monomer used for this invention can use anything, if it melts into water. If the example is given, acrylic acid (meta) and/or its alkali metal salt, Ionicity monomers, such as ammonium salt, 2-(meta)-acrylamide 2-methylsulfonic acid, and/or its

alkali metal salt; (meta) Acrylamide, N and N-dimethyl acrylamide, 2-hydroxyethyl (meta) acrylate, Nonionic monomers, such as N methylol (meta) acrylamide; Diethyl aminoethyl (meta) acrylate, Amino group content unsaturation monomers, the 4th class ghosts of those, etc., such as dimethylaminopropyl (meta) acrylate, can be mentioned, and one sort chosen from these groups or two sorts or more can be used. In addition, the term "an acrylic (meta)" shall mean both an "acrylic" and "methacrylic one" here.

[0019] Acrylic acid (meta) and/or its alkali metal salt, ammonium salt, and acrylamide (meta) are preferably mentioned in these. Although sodium salt, potassium salt, lithium salt, a rubidium salt, etc. are mentioned as an alkali metal salt, the sodium salt from fields, such as performance of the polymer obtained, ease of industrial acquisition, and safety, or potassium salt is desirable.

[0020] Generally the monomer concentration in the aqueous solution of these water solubility ethylene nature unsaturation monomer is 25 weight % - saturated concentration preferably 20weight % or more. Moreover, although acrylic acid (meta), 2-methyl acrylamide 2-sulfonic acid, etc. are used in the form neutralized with the whole-quantity alkali metal compound or the ammonium compound in part the neutralization at this time -- comparatively (the degree of neutralization is called) -- 20-100mol % -- it is 30-100mol % preferably.

[0021] In this invention, you may use a monomer component as of the same kind [ the monomer component used for henceforth / dibasic stage ] as water-soluble above ethylene nature unsaturation monomer kinds as the monomer component used for the first step, or of a different kind. Furthermore, when the monomer component used for henceforth [ dibasic stage ] is as of the same kind as the monomer component used for the first step, monomer concentration, the degree of neutralization, etc. in an aqueous solution may change, and not only arbitrary kinds but various conditions can be adopted.

[0022] (Emulsifier used for the first step) The emulsifier used for the first step of this invention is used for the antiphase suspension-polymerization system of the first step. If these are meltable to a hydrophobic solvent, or a thing which makes a W/O type emulsification system fundamentally with compatibility, they can use anything. Generally HLB is specifically 1-9, and such emulsifiers are less than two to seven non-ion system, and/or an anion system preferably.

[0023] As a concrete example of this emulsifier, sorbitan fatty acid ester, polyoxy sorbitan fatty acid ester, Sucrose fatty acid ester, polyglyceryl fatty acid ester, polyoxyethylene alkyl phenyl ether, Ethyl cellulose, ethyl hydroxyethyl cellulose, oxidation polyethylene, The copolymer of anhydrous mallein-ized polyethylene, anhydrous mallein-ized polybutadiene, an anhydrous mallein-ized ethylene propylene diene terpolymer, alpha olefin, and maleic anhydride or its derivative, polyoxyethylene-alkyl-ether phosphoric acid, etc. are mentioned. The amount of these emulsifiers used is 0.1 to 1% preferably 0.05 to 10weight % to a hydrophobic solvent.

[0024] (Hydrophobic solvent) The hydrophobic solvent used for this invention does not melt into water easily fundamentally, and if inert to a polymerization, it can use anythings. If the example is given, aromatic hydrocarbon, such as alicycle group hydrocarbons, such as aliphatic hydrocarbon, such as n-pentane, n-hexane, n-heptane, and n-octane, cyclohexane, and methylcyclohexane, benzene, toluene, and xylene, etc. will be mentioned. It can see from the stability of industrial acquisition, quality, etc., and can mention as a solvent with desirable n-hexane, n-heptane, and cyclohexane. as opposed to the water-soluble ethylene nature unsaturation monomer aqueous solution with which the amount of these hydrophobic solvent used is used for the first step -- 0.5 - 10 weight twice -- 0.6 - 5 weight twice are adopted preferably.

[0025] (Cross linking agent) In this invention, a cross linking agent can be used for the first step and henceforth [ dibasic stage ] if needed. accepting necessity -- \*\*\*\* -- it is because the self-bridge formation by the monomer itself [ what is called ] occurs and absorptivity resin can form by this, even if a cross linking agent does not exist in this invention according to monomer conditions (the concentration in the kind of monomer, and the aqueous solution of a monomer, the degree of neutralization, etc.). However, if the performance demanded, for example, water absorption power, speed of water absorption, etc. are caused how, a cross linking agent may be required. As a cross linking agent used by this invention, the cross linking agent which has a polymerization nature unsaturated group and/or two or more reactant functional groups is mentioned.

[0026] As a cross linking agent which has two or more polymerization nature unsaturated groups Ethylene glycol, propylene glycol, trimethylol propane, Glycerol polyoxy ethylene glycol, polyoxypropylene glycol, JI of polyols or bird (meta) acrylic ester, such as polyglycerin, The unsaturated polyester obtained by making said polyols and unsaturation acids, such as maleic acid and boletic acid, react Screw acrylamides, such as N and N'-methylene screw acrylamide, JI or bird (meta) acrylic ester obtained by making poly epoxide and acrylic acid (meta) react, The JI (meta) acrylic acid carbamyl ester obtained by making a polyisocyanate and acrylic acid (meta) hydroxyethyl, such as tolylene diisocyanate and hexamethylene di-isocyanate, react An arylation starch, arylation cellulose, diallyl phthalate, other tetra-allyloxy ethane, Multivalent allyl compound systems, such as pentaerythritol bird allyl compound ether, trimethylol propane bird allyl compound ether, diethylene glycol diaryl ether, and triallyl trimellitate, are mentioned. By this invention, also in these, ethylene glycol di(metha)acrylate, Pori ethylene-glycol-di (metha)acrylate, propyleneglycol di(meth) acrylate, Pori propyleneglycol di(meth) acrylate, N, and N'-methylene bis(meta) acrylamide etc. is usually used.

[0027] As a cross linking agent which has two or more reactant functional groups, a diglycidyl ether compound, a HAROEPOKISHI compound, and an isocyanate compound are mentioned, for example. Especially in these, a diglycidyl ether compound is desirable. As an example of a



diglycidyl ether compound Ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, Propylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, glycerol diglycidyl ether, polyglycerin diglycidyl ether, etc. are mentioned. Also in this, ethylene glycol diglycidyl ether is desirable. In addition, as a HAROEPOKISHI compound, epichlorohydrin, EPIBUROMUHI drine compounds, beta-methyl epichlorohydrin, etc. are mentioned, 2, 4-tolylene diisocyanate, hexamethylene di-isocyanate, etc. are mentioned as an isocyanate compound, and it can be used by this invention. The amount of the above cross linking agents used is usually 0.001 to 5 weight % preferably zero to 10weight % to an ethylene nature unsaturation monomer.

[0028] (Water-soluble radical polymerization initiator) The polymerization initiator used for this invention is a water-soluble radical polymerization initiator. As the example, hydrogen peroxide, potassium persulfate, sodium persulfate, Persulfate [, such as ammonium persulfate, ], 2, and 2'-azobis (2-amidinopropane) 2 hydrochloride, They are azo initiators, such as 2 and 2'-azobis (N and N'-dimethylene isobutyl amidine) 2 hydrochloride, 2, and 2'-azobis {2 methyl N-[1 and 1-bis(hydroxymethyl)-2-hydroxyethyl] propione amide}. You may mix and use these water-soluble free-radical initiators. Moreover, hydrogen peroxide and persulfate can be used also as an initiator of a redox type combining reducing substances, amines, etc., such as sulfite and L ascorbic acid. It is appropriate for the amount of these polymerization initiators used to use in 0.01 to 1weight % of the range preferably 0.001 to 5weight % to an ethylene nature unsaturation monomer.

[0029] After the first-step antiphase suspension polymerization is substantially completed in this invention, (Surface active agent) For example, the monomer aqueous solution of eye the dibasic stage is added in the reaction mixture containing water polymer gel grains, and 90% or more of conversion carries out liquid absorption to the first step of water polymer gel grain, after becoming 95% or more preferably, but the surface active agent of this time specification is made to exist. They are these mixtures between the nonionic surface active agent of HLB whose HLB is seven or more and in which the surface active agent which can be used by this invention is more expensive than HLB of said emulsifier, or an anionic surface active agent. The thing usually higher [ one or more ] than HLB of the emulsifier used for the polymerization of HLB of this surface active agent is desirable.

[0030] If the example is given, as a nonionic surface active agent Polyoxyethylene alkyl phenyl ether, Polyoxyethylene alkyl ether, polyoxyethylene fatty acid ester, Polyoxyethylene alkyl phenyl ether, a polyoxyethylene polyoxypropylene blockpolymer, Sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene alkylamine ether, fatty acid diethanolamide, sucrose fatty acid ester, polyglyceryl fatty acid ester, etc. are mentioned.

[0031] As an anionic surface active agent, oleic acid soda, castor oil Cali, Fatty acid salt, such as semi-hardening beef tallow soda, SOJIUMU lauryl sulfate, Higher alcohol sulfate specific salt, a lauryl alcohol sulfate triethanolamine salt, Higher alcohol sulfuric ester salt, such as

lauryl alcohol sulfate ammonium salt, Alkylbenzene sulfonates and alkyl naphthalenesulfonate, such as sodium dodecylbenzenesulfonate and alkyl naphthalene sulfonic acid soda, Dialkyl sulfo succinate, such as a naphthalene sulfonic acid formalin condensate and SOJIUMU dialkyl sulfosuccinate, (\*\*) An alkyl phosphate salt, polyoxyethylene alkyl sulfate soda, Polyoxyethylene sulfate salts, such as polyoxyethylene alkylphenyl sulfate specific salt, Polyoxyethylene polyoxypropylene glycol ethersulfate ammonium salt, polyoxyethylene distyrenated phenyl ether sulfate ammonium salt, and other polymer special anions are mentioned.

[0032] One sort or two sorts or more of mixtures chosen from polyoxyethylene alkyl phenyl ether, a polyoxyethylene polyoxypropylene blockpolymer, and alkylbenzene sulfonates also in the above-mentioned surface active agent are desirable. Moreover, as HLB, nine or more things are desirable. Although the amount of these surface active agents used changes with a monomer kind, other operating conditions to be used, generally it is 0.1 to 5 weight % preferably 0.05 to 10weight % to the absorptivity resin desiccation object after \*\*\*\*\*.

[0033] (Polymerization reaction operation and conditions) In this invention, the first-step antiphase suspension polymerization is first performed for a water-soluble ethylene nature unsaturation monomer aqueous solution under existence of a cross linking agent the bottom of existence of a W/O type emulsifier, and among a hydrophobic solvent using a water-soluble free-radical initiator if needed. Although after the first-step polymerization changes also with polymerization conditions, such as an emulsifier to be used, it serves as a slurry mixture which usually consists of an average of 10 about-300micro hydrous gel, a superfluous emulsifier, and a hydrophobic solvent, and exists. the package polymerization method held by the method of polymerizing at this time teaching a monomer aqueous solution from the beginning to a package in a reactor, or the dropping method which trickles a monomer aqueous solution into a hydrophobic solvent -- any method can be used. This slurry is maintained at a temperature lower than the same temperature or the polymerization temperature as a polymerization of the first step. Subsequently, although said water-soluble ethylene nature unsaturation monomer aqueous solution is added in this slurry and liquid absorption is carried out into water polymer gel, the aforementioned specific surface active agent is made to exist at this time.

[0034] The water-soluble ethylene nature unsaturation monomer aqueous solution of dibasic stage henceforth may be as of the same kind as the first water solubility ethylene nature unsaturation monomer aqueous solution, or different species. For example, when the monomer kinds itself completely differ, it is in the first step at eye the dibasic stage [ the aqueous solution of acrylic acid soda, and ] using the aqueous solution of acrylamide etc. Furthermore, as for a monomer kind, the case where it carries out by the same degree of neutralization which is [ but ] henceforth [ the first step and / dibasic stage ] different with the aqueous solution of combination conditions, for example, acrylic acid soda, or the monomer

concentration in an aqueous solution etc. is mentioned. The amount of monomer aqueous solutions used for henceforth [ dibasic stage ] is 10 to 150 weight % preferably five to 300weight % to the monomer aqueous solution used for the first step. Moreover, in a dibasic stage monomer aqueous solution, neither a cross linking agent nor a water-soluble radical polymerization initiator is necessarily indispensable, and is suitably decided according to a product quality requirement. If a water-soluble radical polymerization initiator in particular is absorbed in slurry of the first step and it is made into a predetermined temperature even if it does not newly put it in into the monomer of dibasic stage henceforth, it will polymerize easily. The important thing at \*\*\*\*\* of a water-soluble ethylene nature unsaturation monomer is carrying out preferably, so that the temperature of the mixture after absorption treatment may become below in the decomposition temperature of a radical polymerization initiator.

[0035] While it adds in slurry or a surface active agent adds a dibasic monomer aqueous solution before adding a dibasic monomer aqueous solution, supplying after adding in a dibasic monomer aqueous solution etc. can carry it out by any method. Addition is made to be able to dissolve or mix with a surface active agent into a dibasic monomer as remaining as it is or an aqueous solution, or can be performed by dissolving or mixing into a hydrophobic solvent. The method of making addition of a surface active agent dissolve or mix into a dibasic monomer aqueous solution, and adding at this invention, is desirable. Although temperature at this time can be carried out at arbitrary temperature, it is desirable for the temperature after liquid absorption to carry out below in polymerization starting temperature, as mentioned above. The temperature which the W/O type emulsifier of the first step which remained in slurry as a slurry temperature dissolves in a hydrophobic solvent mostly is desirable. On the other hand, although the temperature of a dibasic monomer aqueous solution changes according to existence or a kind of a radical polymerization initiator in this aqueous solution etc., generally near a room temperature (i.e., 15 to 40 degree C) is desirable.

[0036] Although it will be in the \*\*\*\*\* slurry state [ according / the whole system / to a liquid absorption gel ] according [ the liquid absorption of a dibasic monomer aqueous solution ] to a cause at very big velocity under existence of the surface active agent of specification as mentioned above, it is important for the liquid absorption of a dibasic monomer at this time to carry out as uniformly as possible. Generally the gel which carried out liquid absorption of the dibasic monomer has the character which is moreover a little easy to condense by tackiness. Therefore, if liquid absorption is uneven or there is liquid absorption nonuniformity, condensation is caused partially, will become a big lump on a part, and it will adhere, or a liquid absorption gel will stagnate, and will have big influence not only on the mean particle diameter and the particle size distribution of a generation granulation article but on continuation manufacture stability. There are various influence factors exerted on liquid absorption homogeneity, and although the kind and concentration of the surface active agent

to be used are natural, temperature, and number of rotations and the feed velocity of a dibasic monomer are also important. Liquid absorption more uniform as number of rotations is high, and as feed velocity is smaller is performed. The method of a suitable example to which uniform monomer liquid absorption is made to perform carrying out number of rotations beyond the number-of-rotations limit in which liquid absorption is possible at first, and lowering little by little is mentioned. Even if this method throws in the monomer aqueous solution of eye the dibasic stage by making number of rotations high enough at first, it is made for the suspension system of the first step to serve as a W/O type. That is, in this state, it is made not to carry out liquid absorption of the dibasic monomer aqueous solution, and the inside of a system is changed into a perfect homogeneous mixing state, emulsion breaking is made to occur and a dibasic monomer aqueous solution is made to absorb uniformly by lowering number of rotations little by little after an appropriate time.

[0037] Although the gel which carried out liquid absorption of the dibasic monomer aqueous solution uniformly by the above operations is made, this gel has the character which is easy to condense like the above-mentioned. Therefore, the number of rotations after liquid absorption is one important factor which determines the mean particle diameter of product granulation. The more the number of rotations at this time is high, the more the mean particle diameter of granulation will become small. If slurry of the gel which carried out liquid absorption uniformly makes a polymerization start by the bottom rise in temperature of churning etc., the grape-like gel to which the approximately spherical gel grains which carried out water adhered mutually will be obtained. The number of rotations at this time is one important factor which determines the mean particle diameter of product granulation grains. Namely, the more it enlarges number of rotations, the more what has small mean particle diameter is obtained.

[0038] When carrying out liquid absorption of the monomer aqueous solution after a dibasic monomer aqueous solution further, it is carried out by the same technique and operation as the method of carrying out liquid absorption of the dibasic monomer aqueous solution fundamentally. Slurry after a polymerization performs a surface treatment etc. if needed through direct dehydration or azeotropy dehydration with a hydrophobic solvent according to a well-known technique, and serves as a product through desiccation, a screen, etc.

[0039]

[Example] Hereafter, although a work example and a comparative example explain this invention concretely, this invention is not limited by these work examples etc. In addition, the water absorption power of absorptivity resin given in these examples, speed of water absorption, particle size distribution/mean particle diameter, and binding hardness are measured by the following methods.

[0040] (1) \*\*\*\* about 0.5g of water-absorption-power absorptivity resin, put into the nylon bag (size of 20cm x 10cm) of 250 meshes, and dip in 500 cc artificial urine for 1 hour. After pulling

up the nylon bag after that and draining off water for 15 minutes, blank amendment of the weight was measured and carried out, and water absorption power was computed according to the following formula.

[0041]

[Equation 1]

$$\text{吸水能} = \frac{\text{膨潤ゲル重量}}{\text{仕込みポリマー量 (g)}}$$

[0042] In addition, the presentation of artificial urine is as follows.

1.94% of artificial urine presentation urea sodium chloride 0.80% calcium chloride 0.06% magnesium sulfate 0.11% pure water 97.09% [0043] (2) 0.9weight % of physiological salines [ 50ml of ] were added to the beaker with a speed of water absorption of 100ml, the rotor (33mm in length) was rotated with the magnetic stirrer, time until a rotor stops was measured after throwing 2g of absorptivity resin into this, and it was considered as speed of water absorption.

[0044] (3) Mean particle diameter / particle-size-distribution ASTM type standard sieve Eight meshes from a top, 12 meshes, 20 meshes, 40 meshes, 60 meshes, It combined in order of 80 meshes, 100 meshes, 150 meshes, 200 meshes, 325 meshes, and a saucer, about 50g of absorptivity resin was put into the best screen, and it was made to shake for 1 minute with a low tap type automatic screen shaker. The rate which carries out the weighing capacity of the weight of the absorptivity resin which remained in each screen, and makes entire volume 100% is computed on a mass basis.

[0045] (4) They are a 20-mesh path - 0.5g of absorptivity resin of a 80-mesh-on cut in 8cm x 8cm of central parts with a binding hardness of 10cm x 10cm of the plate made from SUS. It sprinkles uniformly, and on this, the plate made from SUS further same as the above is put, absorptivity resin is inserted, and the pressure of 130 kgf/cm<sup>2</sup> is put for 10 minutes.

Absorptivity resin after decompression is collected and it is made to shake for 1 minute with said low tap type automatic screen shaker. The quantity which passed 80 mesh sieves is measured and this rate is computed as weight % (it is shown that there is so little crushing of granulation grains that this value is small, i.e., binding hardness is large).

[0046] Cyclohexane 317g was put into the 4 mouth round bottom flask with a capacity of 1l. which attached work-example 1 agitator, the reflux condenser, the thermometer, and the nitrogen gas introduction pipe, the addition dissolution of the sorbitan monostearate 1.587g of HLB=4.7 was carried out, and the bottom internal temperature of nitrogen-gas-atmosphere mind was 20 degrees C at this. Having taken 116.2g of acrylic acid in the conical flask with a capacity of 500 cc independently, and cooling from the exterior, in addition, further, 180.6g of caustic alkali of sodium was added 25%, and 55.7g of water neutralized 70% of the carboxyl

group. The monomer concentration to the water in this case corresponds to 40weight % as monomer concentration after neutralization. Subsequently, further, 0.1104g of hypophosphorous acid soda hydrates were added as a water-soluble chain transfer agent to this, it dissolved in it, and N and N-methylene screw acrylamide 0.0935g and 0.1208g of potassium persulfate could be 20 degrees C at it.

[0047] To 1l. of the aforementioned 4 mouth round bottom flask content, 176.3g of this 500 cc content was added, and churning suspension was carried out. In addition, churning used full zone wings and was performed at 150rpm. Subsequently, when the rise in temperature was carried out at this number of rotations and having been carried out near 55 degree C, the polymerization began and it became a peak near 77 degree C. It held for 15 minutes at 70 degrees C after that. And the temperature of polymerization content was cooled at 50 degrees C after the reaction for 15 minutes.

[0048] Next, said about 176.3g of 500 cc remaining monomer aqueous solutions are taken, This carried out the addition dissolution of the polyoxyethylene polyoxypropylene blockpolymer 1.8g (HLB=10.1, the Toho Chemical Co., Ltd. make, PEPORU B184) as a surface active agent, and it added at the number of rotations of 200rpm to said polymerization content as 20 degrees C. The temperature of the content after addition became about 40 degrees C, the system changed into the existing viscous slurry state a little, and liquid absorption was carried out into the water polymer gel grains of the first step nearly completely after addition completion. Subsequently, when churning was 500rpm and the rise in temperature was carried out, the polymerization began at about 55 degrees C, and it became a peak near 69 degree C. It heated further at this number of rotations after maintenance at 70 degrees C for 15 minutes after that, and dehydrated to 7% to the generated polymer with azeotropy with cyclohexane.

[0049] After the end of dehydration, when churning was stopped, the polymer particle was able to sediment at the bottom of the flask, and decantation was able to separate easily. The separated polymer was heated at 90 degrees C, and adhering cyclohexane and some water were removed. The obtained desiccation polymer was the fine-particles-like agglomerated material which the primary particle been smooth combined in the shape of a grape.

[0050] Fine-particles-like agglomerated material was obtained by this operation and this technique except having used the surface active agent as the polyoxyethylene polyoxypropylene blockpolymer 1.8g (HLB=17, the Dai-Ichi Kogyo Seiyaku Co., Ltd. make, EPAN 485) in work-example 2 work example 1.

[0051] Fine-particles-like agglomerated material was obtained by this operation and this technique except having used the surface active agent as polyoxyethylene nonyl phenyl ether (HLB=17, Dai-Ichi Kogyo Seiyaku Co., Ltd., noy gene EA170) in work-example 3 work example 1.

[0052] Fine-particles-like agglomerated material was obtained by this operation and this

technique except having made the surface active agent into the dodecylbenzenesulfonic acid triethanolamine salt (an anionic surface active agent, the Dai-Ichi Kogyo Seiyaku Co., Ltd. make, the neo gene T) in work-example 4 work example 1.

[0053] Cyclohexane 317g was put into the 4 mouth round bottom flask with a capacity of 1l. which attached work-example 5 agitator, the reflux condenser, the thermometer, and the nitrogen gas introduction pipe, the addition dissolution of the sorbitan monostearate 1.587g of HLB=4.7 was carried out, and the bottom internal temperature of nitrogen-gas-atmosphere mind was 20 degrees C at this. Cooling 116.2g of acrylic acid from the exterior in a conical flask with a capacity of 500 cc independently, in addition, further, 180.6g of caustic alkali of sodium was added 25%, and 55.7g of water neutralized 70% of the carboxyl group. The monomer concentration to the water in this case corresponds to 40weight % as monomer concentration after neutralization. Subsequently, further, 0.1104g of hypophosphorous acid soda hydrates were added as a water-soluble chain transfer agent to this, it dissolved in it, and N and N-methylene screw acrylamide 0.0935g and 0.1208g of potassium persulfate could be 20 degrees C at it.

[0054] This 500 cc content was added to 1l. of the aforementioned 4 mouth round bottom flask content, and churning suspension was carried out. In addition, churning used full zone wings and was performed at 150rpm. Subsequently, when the rise in temperature was carried out at this number of rotations and having been carried out near 55 degree C, the polymerization began and it became a peak near 77 degree C. It held for 15 minutes at 70 degrees C after that. And the temperature of polymerization content was cooled at 52 degrees C after the reaction for 15 minutes.

[0055] Next, 352.5g is made from this operation for the same monomer aqueous solution as said 500 cc, and it is a surface active agent to this. The addition dissolution of the polyoxyethylene nonyl phenyl ether 0.781g (HLB=12, the Dai-Ichi Kogyo Seiyaku Co., Ltd. make, noy gene EA120) was carried out, and it added at the number of rotations of 150rpm to said polymerization content as 20 degrees C. The temperature of the content after addition became about 40 degrees C, the system changed into the existing viscous slurry state a little, and liquid absorption was carried out into the water polymer gel grains of the first step nearly completely after addition completion. Subsequently, when churning was 500rpm and the rise in temperature was carried out, the polymerization began at about 55 degrees C, and it became a peak near 69 degree C. It heated further at this number of rotations after maintenance at 70 degrees C for 15 minutes after that, and dehydrated to 7% to the generated polymer with azeotropy with cyclohexane.

[0056] After the end of dehydration, when churning was stopped, the polymer particle was able to sediment at the bottom of the flask, and decantation was able to separate easily. The separated polymer was heated at 90 degrees C, and adhering cyclohexane and some water

were removed. The obtained desiccation polymer was the fine-particles-like agglomerated material which the primary particle been smooth combined in the shape of a grape.

[0057] Fine-particles-like agglomerated material was obtained by this operation and this technique except having used the surface active agent as 2.6g (an anionic surface active agent, made in Nikko Chemical, NIKKOL ECTD-3NEX) of polyoxyethylene octyl sodium acetate in work-example 6 work example 5.

[0058] Fine-particles-like agglomerated material was obtained by this operation and this technique except having made the surface active agent into 0.39g (an anionic surface active agent, the Dai-Ichi Kogyo Seiyaku Co., Ltd. make, high tenor 12) of Dobanol polyoxyethylene ammonium sulfate salts in work-example 7 work example 5.

[0059] Set in the work-example 8 work example 5. as a surface active agent -- the dodecylbenzenesulfonic acid triethanolamine salt (an anionic surface active agent --) the Dai-Ichi Kogyo Seiyaku Co., Ltd. make and the neo gene T -- 1.8g and a polyoxyethylene polyoxypropylene blockpolymer 0.45g (HLB=10.1 and the Toho Chemical Co., Ltd. make --) Fine-particles-like agglomerated material was obtained by this operation and this technique except having used PEPORU B184, the amount of liquid absorption monomers having been 176.3g, and the number of rotations at the time of liquid absorption having been 400rpm.

[0060] Set in the work-example 9 work example 5. as a surface active agent -- the dodecylbenzenesulfonic acid triethanolamine salt (an anionic surface active agent --) the Dai-Ichi Kogyo Seiyaku Co., Ltd. make and the neo gene T -- 1.8g and a polyoxyethylene polyoxypropylene blockpolymer 0.45g (HLB=17 and the Dai-Ichi Kogyo Seiyaku Co., Ltd. make --) Fine-particles-like agglomerated material was obtained by this operation and this technique except having used EPAN 485, the amount of liquid absorption monomers having been 176.3g, and the number of rotations at the time of liquid absorption having been 400rpm.

[0061] Set in the work-example 10 work example 5. as a surface active agent -- the dodecylbenzenesulfonic acid triethanolamine salt (an anionic surface active agent --) the Dai-Ichi Kogyo Seiyaku Co., Ltd. make and the neo gene T -- 5.99g and a polyoxyethylene polyoxypropylene blockpolymer 1.52g (HLB=10.1 and the Toho Chemical Co., Ltd. make --) Fine-particles-like agglomerated material was obtained by this operation and this technique except having used PEPORU B184, the amount of liquid absorption monomers having been 123.4g, and the number of rotations at the time of liquid absorption having been 400rpm.

[0062] Set in the work-example 11 work example 5. as a surface active agent -- the dodecylbenzenesulfonic acid triethanolamine salt (an anionic surface active agent --) the Dai-Ichi Kogyo Seiyaku Co., Ltd. make and the neo gene T -- 2.38g and a polyoxyethylene polyoxypropylene blockpolymer 0.54g (HLB=10.1 and the Toho Chemical Co., Ltd. make --) Fine-particles-like agglomerated material was obtained by this operation and this technique except having used PEPORU B184, the amount of liquid absorption monomers having been



44.1g, and the number of rotations at the time of liquid absorption having been 300rpm.

[0063] Set in the work-example 12 work example 5. As an emulsifier for the first polymerization, instead of sorbitan monostearate 1.587g The mixture which consists of 0.581g of copolymers and the sorbitan monostearate 1.117g of the alkene 0.537g of carbon numbers 28-38, alkene of these carbon numbers 28-38, and maleic anhydride is used. the first polymerization number of rotations shall be 180rpm -- as a surface active agent -- the dodecylbenzenesulfonic acid triethanolamine salt (an anionic surface active agent --) the Dai-ichi Kogyo Seiyaku Co., Ltd. make and the neo gene T -- 1.8g and a polyoxyethylene polyoxypropylene blockpolymer 0.45g (HLB=10.1 and the Toho Chemical Co., Ltd. make --) Fine-particles-like agglomerated material was obtained by this operation and this technique except having used PEPORU B184, the amount of liquid absorption monomers having been 176.3g, and the number of rotations at the time of liquid absorption having been 400rpm.

[0064] Cyclohexane 325.4g was put into the 4 mouth round bottom flask with a capacity of 1l. which attached work-example 13 agitator, the reflux condenser, the thermometer, and the nitrogen gas introduction pipe, the addition dissolution of the sorbitan monostearate 1.627g of HLB=4.7 was carried out, and the bottom internal temperature of nitrogen-gas-atmosphere mind was 20 degrees C at this. Cooling 116.2g of acrylic acid from the exterior in a conical flask with a capacity of 500 cc independently, in addition, further, 206.6g of caustic alkali of sodium was added 25%, and 38.74g of water neutralized 80% of the carboxyl group. The monomer concentration to the water in this case corresponds to 40weight % as monomer concentration after neutralization. Subsequently, further, 0.1104g of hypophosphorous acid soda hydrates were added as a water-soluble chain transfer agent to this, it dissolved in it, and N and N-methylene screw acrylamide 0.0935g and 0.1208g of potassium persulfate could be 20 degrees C at it.

[0065] This 500 cc content was added to 1l. of the aforementioned 4 mouth round bottom flask content, and churning suspension was carried out. In addition, churning used full zone wings and was performed at 180rpm. Subsequently, when the rise in temperature was carried out at this number of rotations and having been carried out near 56 degree C, the polymerization began and it became a peak near 78 degree C. It held for 15 minutes at 70 degrees C after that. And the temperature of polymerization content was cooled at 52 degrees C after the reaction for 15 minutes.

[0066] Independently, cooling 151.1g of acrylic acid from the exterior in a conical flask with a capacity of 500 cc, in addition, 206.6g of caustic alkali of sodium was added 25%, and 38.74g of water neutralized 61.5% of the carboxyl group further. The monomer concentration to the water in this case corresponds to 45.2weight % as monomer concentration after neutralization. Subsequently, further, 0.1104g of hypophosphorous acid soda hydrates were added as a water-soluble chain transfer agent to this, it dissolved in it, and N and N-methylene screw

acrylamide 0.0935g and 0.1208g of potassium persulfate could be 20 degrees C at it. 319.4g of this monomer aqueous solution was taken, this carried out the addition dissolution of the polyoxyethylene nonyl phenyl ether 0.801g (HLB=12, the Dai-Ichi Kogyo Seiyaku Co., Ltd. make, noy gene EA120) as a surface active agent, and it added at the number of rotations of 150rpm to said polymerization content. The temperature of the content after addition became about 40 degrees C, the system changed into the existing viscous slurry state a little, and liquid absorption was carried out into the water polymer gel grains of the first step nearly completely after addition completion. Subsequently, when churning was 500rpm and the rise in temperature was carried out, the polymerization began at about 55 degrees C, and it became a peak near 69 degree C. It heated further at this number of rotations after maintenance at 70 degrees C for 15 minutes after that, and dehydrated to 7% to the generated polymer with azeotropy with cyclohexane.

[0067] After the end of dehydration, when churning was stopped, the polymer particle was able to sediment at the bottom of the flask, and decantation was able to separate easily. The separated polymer was heated at 90 degrees C, and adhering cyclohexane and some water were removed. The obtained desiccation polymer was the fine-particles-like agglomerated material which the primary particle been smooth combined in the shape of a grape.

[0068] In work-example 14 work example 13, it is 240.0g about the amount of liquid absorption monomer aqueous solutions, as a surface active agent -- the dodecylbenzenesulfonic acid triethanolamine salt (an anionic surface active agent --) 3.8g and a polyoxyethylene polyoxypropylene blockpolymer 0.86g (HLB=10.1, the Toho Chemical Co., Ltd. make, PEPORU B184) were used for the Dai-Ichi Kogyo Seiyaku Co., Ltd. make and the neo gene T, and fine-particles-like agglomerated material was obtained by this operation and this technique except liquid absorption number of rotations having been 500rpm.

[0069] A surface active agent was not added in the liquid absorption monomer aqueous solution in comparative example 1 work example 5, but the monomer aqueous solution was added to the first polymerization content, and polymerization and dehydration were performed by this operation and this technique. The obtained desiccation polymer was the simple grain-like fine-particles-like polymer which included fines considerably.

[0070] Based on the technology of a description, it retested to comparative example 2 JP,H3-227301,A. That is, Cyclohexane 317g was put into the 4 mouth round bottom flask with a capacity of 1l. which attached the agitator, the reflux condenser, the thermometer, and the nitrogen gas introduction pipe, the addition dissolution of the sorbitan monostearate 1.587g of HLB=4.7 was carried out, and the bottom internal temperature of nitrogen-gas-atmosphere mind was 20 degrees C at this. Cooling 116.2g of acrylic acid from the exterior in a conical flask with a capacity of 500 cc independently, in addition, further, 180.6g of caustic alkali of sodium was added 25%, and 55.7g of water neutralized 70% of the carboxyl group. The

monomer concentration to the water in this case corresponds to 40weight % as monomer concentration after neutralization. Subsequently, further, 0.1104g of hypophosphorous acid soda hydrates were added as a water-soluble chain transfer agent to this, it dissolved in it, and N and N-methylene screw acrylamide 0.0935g and 0.1208g of potassium persulfate could be 20 degrees C at it.

[0071] To 1l. of the aforementioned 4 mouth round bottom flask content, 176.3g of abbreviation halves of this 500 cc content were added, and churning suspension was carried out. In addition, churning used full zone wings and was performed at 150rpm. Subsequently, when the rise in temperature was carried out at this number of rotations and having been carried out near 55 degree C, the polymerization began and it became a peak near 77 degree C. It held for 15 minutes at 70 degrees C after that. And the temperature of polymerization content was cooled at 20 degrees C after the reaction for 15 minutes, and sorbitan monostearate of the emulsifier was deposited.

[0072] Next, said about 176.3g of 500 cc remaining monomer aqueous solutions were taken, and it added at the number of rotations of 50rpm to said polymerization content as 20 degrees C, and held at this temperature for 1 hour. Subsequently, when churning was 150rpm and the rise in temperature was carried out, the polymerization began at about 55 degrees C, and it became a peak near 69 degree C. It heated further at this number of rotations after maintenance at 70 degrees C for 15 minutes after that, and dehydrated to 7% to the generated polymer with azeotropy with cyclohexane.

[0073] After the end of dehydration, when churning was stopped, the polymer particle was able to sediment at the bottom of the flask, and decantation was able to separate easily. The separated polymer was heated at 90 degrees C, adhering cyclohexane and some water were removed, and fine-particles-like polymer was obtained.

[0074] Fine-particles-like polymer was obtained by this operation and this technique except the number of rotations in the first polymerization having been 170rpm in comparative example 3 comparative example 2, and each of temperature of the polymerization content after a polymerization reaction and temperature of the liquid absorption monomer aqueous solution having been 13 degrees C.

[0075] Based on the technology of a description, it retested to comparative example 4 JP,H3-227301,A. namely, -- putting n-heptane 376.2g into a 4 mouth round bottom flask with a capacity of 1l. which attached the agitator, the reflux condenser, the thermometer, and the nitrogen gas introduction pipe -- this -- 1.38g (the product made from Mitsubishi Kasei Food --) of sucrose fatty acid ester of HLB=3 Ryoto sugar ester S-370 is added and it is 50 degrees C. The rise in temperature was carried out, it dissolved and the bottom internal temperature of nitrogen-gas-atmosphere mind was 30 degrees C. Cooling 80.6g of acrylic acid from the exterior in a conical flask with a capacity of 500 cc independently, in addition, further, 179.1g of

caustic alkali of sodium was added 25%, and 21.3g of water neutralized 70% of the carboxyl group. The monomer concentration to the water in this case corresponds to 40weight % as monomer concentration after neutralization. Subsequently, N and N-methylene screw acrylamide 0.059g and 0.0765g of potassium persulfate added 0.069g of hypophosphorous acid soda hydrates to this as a water-soluble chain transfer agent further, and it dissolved in it, and could be 20 degrees C.

[0076] This 500 cc content was added to 1l. of the aforementioned 4 mouth round bottom flask content, and churning suspension was carried out. In addition, churning used full zone wings and was performed at 225rpm. Subsequently, when the rise in temperature was carried out at this number of rotations and having been carried out near 68 degree C, the polymerization began and it became a peak near 84 degree C. It held at 70 degrees C after that for 1 hour, and the polymerization was completed. Next, the temperature of polymerization content was cooled at 20 degrees C, and the emulsifier was deposited.

[0077] Next, 281.2g of the same monomer aqueous solutions as this first step were made, and it added at the number of rotations of 150rpm to said polymerization content as 20 degrees C, and held for 30 minutes at this temperature. Liquid absorption of the added monomer aqueous solution was carried out mostly. Subsequently, when churning was 500rpm and the rise in temperature was carried out, the polymerization began at about 67 degrees C, and it became a peak near 75 degree C. It heated further at this number of rotations after maintenance at 70 degrees C after that for 1 hour, and dehydrated to 7% to the generated polymer with azeotropy with n-heptane.

[0078] After the end of dehydration, when churning was stopped, the polymer particle was able to sediment at the bottom of the flask, and decantation was able to separate easily. The separated polymer was heated at 90 degrees C, and adhering n-heptane and some water were removed. Fine-particles-like polymer was obtained. It evaluated per mean particle diameter, particle size distribution, and binding hardness about the polymer obtained above by work examples 1-14 and comparative examples 1-4. The result is shown in Table 1.

[0079] Fine-particles-like agglomerated material obtained in work-example 15 work example 10 was made into 20 weight % of moisture, 1000 ppm of gamma-glycidoxypyrroltrimetoxysilane was added to the resin desiccation object for absorptivity as a finishing agent, surface bridge formation was performed, and after-desiccation fine-particles-like agglomerated material was obtained.

[0080] AP-200N (product made from Japanese Synthesis) and SA60 of the commercial item (made by Sumitomo Seika Chemicals Co., Ltd.) were made into comparative examples 5 and 6, respectively in the granulation article obtained considering the comparative example 5 and 6 antiphase suspension-polymerization method as a base. It evaluated per water absorption power and speed of water absorption above about the polymer of a work example 15 and

comparative examples 5-6. The result is shown in Table 2.

[0081] As shown in work examples 1-14 and comparative examples 1-4 (Table 1) above, by using a specific surface active agent in this invention, the hardness of the agglomerated material which liquid absorption of the dibasic monomer aqueous solution was performed very efficiently, and was obtained is large, and particle size distribution is also narrow, and there are few particle components (#80 path article). Moreover, especially the absorptivity resin granulated body obtained by this invention as shown in a work example 15 and comparative examples 5-6 is understood that speed of water absorption is early.

[0082]

[Table 1]

表 1

実施例／ 比較例	平均粒径 ( $\mu$ )	粒径分布 (重量%)			結着強度 (重量%)
		#20以上	#20未満～#80未満	#80未満	
実施例 1	1015	58.8	40.3	0.9	2.5
2	1300	73.5	26.5	0.0	3.4
3	700	37.8	58.7	3.5	3.8
4	670	34.4	63.8	1.8	4.0
5	590	30.4	64.4	5.2	8.2
6	450	16.6	77.4	6.0	4.2
7	705	41.6	55.8	2.6	7.2
8	500	20.4	76.8	2.8	4.6
9	420	7.9	88.6	3.5	7.3
10	335	23.0	70.1	6.9	5.8
11	620	33.2	64.2	2.6	3.9
12	705	45.2	51.6	3.3	4.5
13	370	0.8	93.2	6.0	6.8
14	770	46.2	53.2	0.6	2.1
比較例 1	造粒せず				
2	185	2.2	48.2	49.6	15.1
3	260	12.9	66.7	20.4	12.2
4	160	4.1	36.1	59.8	10.3

[0083]

[Table 2]

表 2

実施例／比較例	吸水能 ( g / g )	吸水速度 ( 秒 )
実施例 1 5	5 0	2 8
比較例 5	4 6	4 0
比較例 6	5 0	4 2

[0084]

[Effect of the Invention] According to this invention, it can manufacture by low cost by the operation in which the agglomerated material which has the above features which are not in the former is very plain by making said specific surface active agent exist in the reaction mixture containing the water polymer gel grains obtained by antiphase suspension polymerization, and carrying out liquid absorption of the dibasic monomer aqueous solution. And such a thing is suitable for a disposable diaper, a sanitary napkin, and the water retention agent for soil, for example.

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[Translation done.]